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(54) Title: PIGMENT MATERIALS AND THEIR PREPARATION AND USE
(54) Titre: MATIERES PIGMENTAIRES; PREPARATION ET UTILISATION ASSOCIEES

(57) Abstract

A method of preparing and using a composite pigment material which incorporates a fine particulate material, which method comprises the steps of: (a) treating an aqueous medium containing dispersed particles of a fine particulate material by chemically reacting therein a first reactant and a second reactant to precipitate therein crystals of a white insoluble pigment compound thereby forming in the aqueous medium a composite pigment material comprising a composite matrix of precipitated crystals of the white pigment compound and particles of the fine particulate material dispersed and bonded within the matrix wherein the first and second reactants are such that they react together without producing a substantial amount of non-crystalline by-product; and (b) adding the composite material to a composition for forming or coating a fibrous sheet material. The method may thereafter include (c) forming or coating a fibrous sheet material using the composition incorporating the composite material. The said aqueous medium employed in step (a) may comprise an aqueous suspension or slurry.

(57) Abrégé

L'invention concerne un procédé de préparation et d'utilisation d'une matière pigmentaire composite comprenant une matière à fines particules. Le procédé de préparation comprend les étapes suivantes: (a) traiter un milieu aqueux contenant des particules dispersées d'une matière à fines particules par réaction chimique avec un premier réactif et un second réactif de manière à précipiter des cristaux d'un composé pigmentaire insoluble blanc afin de former, dans ce milieu aqueux, une matière pigmentaire composite comprenant une matrice composite formée, d'une part, de cristaux précipités du composé pigmentaire blanc et, d'autre part, de particules de la matière à fines particules, laquelle matrice est dispersée et liée à l'intérieur même de la matrice; le premier réactif et le second réactif étant tels qu'ils réagissent ensemble sans produire une quantité significative de sous-produit non cristallin; et (b) ajouter la matière composite à une composition de manière à former ou à recouvrir un matériau en feuille fibreux. Le procédé de fabrication peut également comprendre une étape consistant à (c) former ou recouvrir un matériau en feuille fibreux à l'aide d'une composition contenant la matière composite. Le milieu aqueux utilisé lors de l'étape (a) peut comprendre une suspension aqueuse ou une pâte.

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(71) Applicant (for all designated States except US): IMERYS
PIGMENTS, INC. [US/US]; Suite 300, 100 Mansell
Court East, Roswell, GA 30076 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): RODRIGUEZ,
Jose, Maria [US/US]; 107 Whippoorwill Court, SE,
Eatonton, GA 31024 (US). REY, Paul [US/US]; 2205
Shafer Vue Drive, Coraopolis, PA 15108 (US).

(74) Agents: GARRETT, Arthur, S. et al.; Finnegan, Hen-
derson, Farabow, Garrett & Dunner, L.L.P., 1300 I Street,
N.W., Washington, DC 20005-3315 (US).

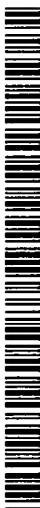
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(54) Title: PIGMENT MATERIALS AND THEIR PREPARATION AND USE

(57) Abstract: A method of preparing and using a composite pigment material which incorporates a fine particulate material, which method comprises the steps of: (a) treating an aqueous medium containing dispersed particles of a fine particulate material by chemically reacting therein a first reactant and a second reactant to precipitate therein crystals of a white insoluble pigment compound thereby forming in the aqueous medium a composite pigment material comprising a composite matrix of precipitated crystals of the white pigment compound and particles of the fine particulate material dispersed and bonded within the matrix wherein the first and second reactants are such that they react together without producing a substantial amount of non-crystalline by-product; and (b) adding the composite material to a composition for forming or coating a fibrous sheet material. The method may thereafter include (c) forming or coating a fibrous sheet material using the composition incorporating the composite material. The said aqueous medium employed in step (a) may comprise an aqueous suspension or slurry.

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TITLE OF THE INVENTION

Pigment materials and their preparation and use

BACKGROUND OF THE INVENTION

The present invention relates to pigment materials and their preparation and use. In particular, it relates to new pigment material comprising a composite containing a fine particulate material such as titanium dioxide and to the preparation of such material and its use in operations to make or coat paper and the like sheet materials.

Titanium dioxide, herein "TiO₂", is an example of a fine particulate material which, unlike materials which are employed as bulk fillers, is employed for a specific function in paper making and paper coating operations. It offers excellent pigment opacity and brightness (which together result in excellent light scattering) and is therefore used to extend these properties in a paper making or coating composition. TiO₂ is a very expensive material and is consequently used only sparingly in paper making or coating compositions, eg usually forming less than 5% by weight of the solids present in the composition. Because of its cost, TiO₂ needs to be employed as efficiently as possible.

The optimum particle size for TiO₂ pigment particles to give the best light scattering properties has been determined in the prior art to be about 0.2µm to 0.3µm. TiO₂ pigment material is normally supplied commercially in a form wherein the

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10 particles have this optimum size. The TiO_2 product may be supplied dry, in which case it requires dispersion in liquid media to wet and to deagglomerate or disperse the particles.

5 Alternatively, TiO_2 may be supplied commercially in a pre-dispersed slurry form which may incorporate a relatively large amount of anionic stabiliser.

15 Since the TiO_2 particles employed in paper making are very fine and are usually dispersed with relatively high levels of dispersant to make slurries containing the material pumpable and to maximise the spacing between particles to give optimal light scatter, it is difficult to retain such particles when they are employed in a furnish or like composition in a paper or like sheet forming operation.

20 In order to improve TiO_2 retention in such operations, in order to minimise TiO_2 losses, various chemical retention aids are employed in the prior art. In general, such aids are expensive chemicals, eg water soluble polymers, and the extent of use of such chemicals employed for the conventional retention of TiO_2 is considered to be very costly. Where the TiO_2 is supplied with anionic stabiliser large amounts of cationic chemicals (which may also serve as or be delivered together with retention aids) may be required to reduce the anionic loading.

25 TiO_2 particles (when used in a pigment-containing composition) have a tendency to agglomerate especially at higher loading levels, this effect being known as 'crowding'. Use of retention aid

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10 chemicals can increase crowding which has been demonstrated in the prior art to have an adverse effect on the light scattering efficiency of the particles. This can result in degradation of the
15 expected optical properties of commercially available TiO_2 material when used as a particulate pigment material in paper.

20 Furthermore, such added chemicals when used in substantial quantities to improve TiO_2 retention, have an adverse effect on the formation of the paper or
25 other sheet being produced and can result in sheets of less than ideal quality in which the constituents of the sheet are not uniformly distributed.

30 Attempts have been reported in the prior art to counteract the effects of crowding of fine
35 particulate material, especially TiO_2 , by forming composites of the particles of the material to space the particles from one another. These attempts have
40 been aimed primarily at improving the optical properties of the compositions to which the composite material is added.

45 One method of the prior art which involves titanium dioxide TiO_2 , is described in US Patent No 2,170,800 wherein a mixture of TiO_2 and CaSO_4 is
50 reacted with a solution of Na_2CO_3 to convert CaSO_4 to CaCO_3 and precipitate a composite pigment comprising TiO_2 and CaCO_3 . Another method for producing a TiO_2 - CaCO_3 composite pigment is described in US Patent No 3,528,838 in which a solution of Na_2CO_3 and a solution
55 of CaCl_2 are employed. Pigmentary TiO_2 is dispersed in one of these solutions and the two solutions are

5 mixed to precipitate a TiO_2 - CaCO_3 composite pigment.

10 Still another coalesced composite pigment is

described in US Patent No 3,832,206 wherein

15 pigmentary TiO_2 is dispersed in a solution of Na_2CO_3 .

5 A slurry of $\text{Ca}(\text{OH})_2$ is added to the Na_2CO_3 - TiO_2 mixture

15 in order to react with the Na_2CO_3 and precipitate

CaCO_3 . The CaCO_3 formed in the presence of the TiO_2

pigment particles results in a coalesced composite

20 pigment of TiO_2 - CaCO_3 . In each of these three prior

10 art processes, the composite pigment product must,

before it can be used in paper making, be separated

from the aqueous phase in which it is formed and

25 washed free of the by-product resulting from the

chemical reaction involved in producing CaCO_3 . This

15 by-product is Na_2SO_4 in case of US Patent No

2,170,800, NaCl in case of US Patent No 3,528,838 and

30 NaOH in case of US Patent No 3,832,206. Removing the

by-product in each case is time consuming and costly.

In US Patent No 4,028,173, Olson describes the

20 use of a physical mixture of CaCO_3 and TiO_2 in the

manufacture of papers.

35 Another avenue of producing carbonate

agglomerates consists of utilizing organic chemicals

or silicates to bind the aggregates. The following

25 prior published patents disclose the use of such

40 binders. In US Patent No 4,072,537, to F L Kurrle, a

composite silicate pigment is prepared by a

precipitation reaction employing an aqueous

45 suspension of clay particles wherein spherical

30 hydrous metal silicates particles are precipitated on

the planar surface of the clay. In US Patent No

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4,816,074 by Ravthatha et al, a process is described in which a structured aggregated kaolin pigment is prepared by mixing substantially dry kaolin in particulate form with an aqueous alkali metal silicate to deposit on the surface of the kaolin particles a substantially molecular level of said silicate without formation of silica gel, drying the treated kaolin without calcination and exposing it to an acidic gas. The product is useful as a pigment in the coating or filling of paper. In a further aspect of the invention, it is preferable to intermix with the kaolin feed, small quantities of an aggregation agent. Such agent is selected from one or more members of the group consisting of the alkaline earth metal carbonate, chlorides or hydroxides or lithium carbonate.

Polyacrylate alkali metal salts are known as dispersants for clay, eg kaolin. Sodium polyacrylate is a common dispersant, frequently used in the refining/working up the crude material. However, US Patent No 5,082,887 describes a pigment composition for the coating and filling of paper comprising a dispersion of an aqueous phase, a pigment or mixture of pigments such as kaolin, titanium dioxide and calcium carbonate, gypsum, mica and a dispersing agent comprised of carboxyl-containing polymers, eg an acrylic polymer, at least 60% of which is converted to the salt form with a polyvalent cation, calcium, and if desired the balance may be converted with a monovalent cation such as sodium, ammonium and quaternary amine cations. Gaseous carbon dioxide is

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added to the slurry, and reacts, with the remaining calcium ion to precipitate calcium carbonate onto the polymeric carboxyl calcium salt. The resultant composite aggregates are recovered and dried, as product.

The problem of maintaining a reasonable retention of TiO_2 particles in a paper making operation, whilst at the same time avoiding agglomeration or crowding and an adverse effect on formation caused by the addition of chemicals to facilitate retention, has not satisfactorily been solved in the prior art. One purpose of the present invention is to provide a novel solution to this problem.

Similar problems arise with the retention of other fine particulate materials, and it is another purpose of the present invention to provide a novel solution to the retention of such materials.

It is a further purpose of this invention to produce a novel pigment material which is useful in paper coating.

In the light of the foregoing, it may also be regarded as an object of the present invention, to provide a structural composite pigment, such as a composite titanium dioxide/calcium carbonate, kaolin/calcium carbonate, alumina/calcium carbonate, silica/calcium carbonate, mica/calcium carbonate, gypsum/calcium carbonate which possesses improved light scattering characteristics, and hence is useful as an opacifier and light scattering filler for paper and paper products, and which may similarly be used

in other paper manufacturing applications, including
in the coating of the same.

It is yet a further object of the present
invention, to provide a method for producing
structured composite mineral pigments as
aforementioned, which consists of a minimal number of
simply conducted steps, which utilize relatively
simple and inexpensive apparatus.

It is a further object of the present invention,
to provide a method for producing a pigment with good
retention properties in the paper web of the
expensive component of the aggregate pigment.
Furthermore, the method provides a pigment without
subjecting to any purification or calcination step.

It is yet a further object of the present
invention, to provide a pigment with a cationic zeta
potential which decreases charge demand as compared
to anionic or anionic dispersed pigments of the prior
art.

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SUMMARY OF THE INVENTION

The above purposes and objects and others which
will become apparent from this specification are met
by the present invention.

The present invention is concerned with a method
for the preparation and use of structured composite
pigments, which can, amongst other things, improve
the retention of fine particulate material such as
TiO₂ in paper making compositions without seriously
affecting optical or other properties, in some cases
beneficially improving such properties also. The

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resulting composite pigments can also be used
beneficially in paper coating.

According to the present invention in a first
aspect there is provided a method of preparing and
5 using a composite pigment material which incorporates
a fine particulate material, which comprises (a)
15 treating an aqueous medium containing dispersed
particles of a fine particulate material by
chemically reacting therein a first reactant and a
10 second reactant to precipitate therein crystals of a
white insoluble pigment compound thereby forming in
the aqueous medium a composite matrix of precipitated
crystals of the white pigment compound and particles
25 of the fine particulate material dispersed and bonded
within the matrix wherein the first and second
reactants are such that they react together without
producing a substantial amount of non-crystalline by-
product; and (b) adding the composite material to a
30 composition for forming or coating a fibrous sheet
material. The method may thereafter include (c)
forming or coating a fibrous sheet material using the
35 composition incorporating the composite material.
The said aqueous medium employed in step (a) may
comprise an aqueous suspension or slurry.
25 The fine particulate material and the first and
second reactants employed to produce the
precipitation reaction may be obtained from separate
stocks and may be added together prior to step (a) to
40 produce the composite pigment material. Either or
45 both of these materials may be in dry or wet (eg
slurry) form when they are added together.

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At least part of the fine particulate material may comprise fresh particles. By 'fresh' particles of fine particulate material is meant particles which have not previously been used in a sheet forming or coating or other operation.

The fibrous sheet material formed or coated in step (c) may comprise paper, paper board, card, cardboard, laminated paper and the like herein collectively called 'paper', wherein the fibrous sheet material comprises organic, eg cellulosic fibres, and in many cases also inorganic filler comprising a particulate pigment material.

By "fine particulate material" is meant a particulate material wherein the particles have a size distribution such that at least 90% by weight have an esd (equivalent spherical diameter as measured in a known way by sedimentation) of less than $2\mu\text{m}$. At least 50 per cent by weight may have an esd less than $1\mu\text{m}$. The mean particle size of the particles of the fine particulate material may for example be in the range $0.1\mu\text{m}$ to $1.5\mu\text{m}$ especially $0.1\mu\text{m}$ to $0.7\mu\text{m}$. The fine particulate material will generally be one which is more expensive than bulk filler materials (eg conventional kaolin and/or calcium carbonate) and one which is used in paper for a specific function (other than bulk filling) and generally has a poor natural retention in paper making.

The present invention is especially beneficial where the fine particulate material comprises TiO_2 , although the particulate material may alternatively,

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or in addition, be selected from calcined kaolin, fine silica, eg so called fumed silica, sodium silicate, aluminium silicate, sodium aluminium silicate, talc, calcium sulfate, alumina, mica and so called plastic pigment materials, eg produced from melamine formaldehyde and mixtures of these materials. It should be noted that calcined material may contain aggregates of fine particles fused or sintered together but the fine particles which make up such aggregates may have the required particle size distribution properties if measured individually.

The said white insoluble pigment compound which is precipitated in the method according to the first aspect of the present invention may comprise a water insoluble salt, ie it may be formed from or regarded as formed from an acid and a base. It may comprise a simple salt formed from a single anion and a single cation. It may conveniently comprise an alkaline earth metal carbonate, eg calcium carbonate, produced by reacting carbon dioxide with a suitable hydroxide, eg calcium hydroxide. Reactants (eg providing acidic and basic species) to produce the white insoluble pigment compound may be added together or separately to the aqueous medium.

DESCRIPTION OF THE INVENTION

The composite pigment material according to the present invention comprises a fine particulate material dispersed and bonded within a matrix formed of crystals of a precipitated white insoluble

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10 inorganic compound, eg calcium carbonate. The parent application, US Serial No 08/957,280 describes such a composite material but in that case a substantial amount of fibers are also added to the aqueous
15 suspension to be contained within the composite matrix. The production of material according to the present invention need not include deliberate addition of fibers, although in one embodiment of the invention the aqueous medium in which the precipitate
20 crystals are formed may contain fibers already present, eg the aqueous medium may comprise white water from a paper making operation.

25 By the method of the invention, the particles of the fine particulate material, if suitably dispersed
15 when the precipitation reaction is carried out, unexpectedly and beneficially remain dispersed in the solid composite matrix formed when the bonding
30 crystals of the white pigment compound are precipitated and become cemented to the bonding
20 crystals.

35 Where the precipitate compound formed is a basic compound, eg calcium carbonate, it can advantageously be effective in neutralizing any anionic charges present in a paper making or coating composition, eg
25 due to the addition of anionic stabilisers, thereby
40 allowing the amount of any added cationic chemicals to be reduced.

45 Particulate materials to be used as fillers in paper making usually carry a surface charge when
30 dispersed in water. The surface charge is dependent on pH and chemical species at the crystal surface.

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The zeta potential is a convenient known way to measure the charge at the plane of shear near the crystal surface. Precipitated calcium carbonate is one of the few fillers having a positive zeta potential. It is well known, eg from "Retention of Fines and Fillers During Papermaking, Precipitated Calcium Carbonate", Chapter 14 by J M Gess (TAPPI Press, Atlanta, GA) that the charge on the surface of the filler particle has a dramatic influence on first pass retention. Positively charged fillers are retained better than negatively charged fillers.

By forming a composite material comprising particles of fine particulate material such as TiO_2 , and/or one of the other materials referred to earlier, dispersed and bonded within a solid matrix of crystals of white pigment compound, a new pigment structure is provided which can show various unexpected benefits when used in paper making or paper coating operations as described hereinafter.

According to the present invention in a second aspect there is provided a composite pigment material comprising a composite matrix of precipitated crystals of white pigment compound and particles of fine particulate material as defined hereinbefore, dispersed and bonded within the matrix which composite material is the product of step (a) of the method according to the first aspect.

Particles of the composite pigment material according to the second aspect may be employed in a known manner as a pigment filler ingredient in papermaking or as a pigment ingredient in paper

5 coating. Such particles may be the sole filler or
10 pigment source or they may optionally be blended with
conventional or known fillers or pigment particles
employed in such applications, eg selected from one
5 or more of kaolin, calcined kaolin, calcium carbonate
15 (derived from a natural or synthetic source or
composited in a known manner with other materials, eg
derived from waste streams), dolomite, talc, mica or
untreated TiO_2 or other fine particulate material (eg
20 as used in the preparation of the composite pigment
material).

The composite pigment material according to the
second aspect of the present invention may form from
25 1% to 100% by weight of the filler or pigment
15 particles employed in such applications, eg in the
making of a furnish employed in paper making or a
coating composition employed in paper coating, or in
30 specialist sheet coating operations, eg decorative
laminate formation, although it may be blended with
20 other, eg conventional filler or pigment, materials
eg wherein it may form up to 50% by weight, in some
35 cases up to 80% by weight of the blend. The
filler(s) or pigment(s) employed in such applications
will depend upon the use of the filler or pigment.
25 Fillers in papermaking may form up to 40 per cent by
40 weight (on a dry solids weight basis) of the paper
making composition or furnish. The pigment(s)
employed in coating compositions usually forms up to
45 80% by weight in some cases as high as about 95% (on
30 a dry solids basis) by weight of the composition.

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The composite pigment material according to the second aspect of the present invention can allow fine particulate materials such as TiO_2 and the other materials referred to earlier to be much more efficiently retained in a paper making operation. For example, in contrast to the low retention levels obtained in the prior art for untreated TiO_2 (without application of a retention aid) or for TiO_2 treated with only a small amount of retention aid (eg retention levels of about 30% or less, even 20% or less, as illustrated hereinafter), the retention level of TiO_2 for a single pass in a paper sheet making operation by production and use of the composite material according to the second aspect of the present invention can advantageously be much greater as illustrated hereinafter (depending on the composition of the composite pigment material and the amount of the material loaded into the paper composition). This allows a reduction in the quantity and cost of retention aid chemical(s) employed to retain fine particulate material such as TiO_2 , although some retention aid chemical(s) may optionally be added, (eg in the usual manner to the dilute pulp furnish stock from which the paper sheets are to be produced).

Beneficially, reducing the amount of retention aid chemicals can also improve the burst strength (also known as burst index) of the sheet produced and the paper sheet formation, ie the overall quality of the paper sheet produced by providing more uniform distribution of the constituents of the sheet.

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10 In addition, the sheet so formed may
beneficially have a stiffness or 'crackle' which is
greater than that for a comparable sheet made from
fine particulate material such as TiO_2 as in the prior
5 art. This allows, for example, paper of the same
stiffness as comparable prior art sheets to be
15 produced lighter in weight and (for sheets of the
same weight as prior art sheets) more cheaply.

20 Furthermore, because the fine particulate
10 material is better retained in the paper making
process, less fine particulate material is lost and
it is not necessary to compensate for the usual loss
which is expected to occur by addition of excessive
25 quantities of the material, which, as in the case of
15 TiO_2 , can be very expensive.

30 A further benefit obtained by preparation and
use of composite pigment material according to the
second aspect of the present invention in a paper
making or coating operation is that the undesirable
20 crowding (normally obtained as in the prior art) of
particles of the fine particulate material caused or
35 exacerbated by use of added chemicals is reduced and
this allows the adverse effect on scattering of light
from the particles caused by such crowding to be
25 reduced. Since the crystals of the precipitated
40 pigment compound may themselves be fine and highly
scattering their presence contributes beneficially to
the optical properties of the composite pigment
45 material and may allow further reduction of the
30 amount of fine particulate material, where pigment
material such as TiO_2 , which may be employed as

5 compared with prior art compositions aimed at giving
10 similar properties.

Thus, generally the present invention allows
savings in the amount and cost of fine particulate
5 material employed in paper making and paper coating
as well as in the use of associated expensive
15 chemicals as well as providing improvements in
various properties of the sheet product.

According to the present invention in a third
20 aspect there is provided a paper or like sheet
material incorporating filler or coating pigment
particles which comprise particles of the composite
pigment material according to the second aspect
25 defined earlier.

15 Surprisingly and beneficially the formation and
use of a composite pigment material in accordance
with the invention allows certain optical properties,
30 particularly scattering, of a paper sheet made or
coated with a composition containing the composite
20 pigment material according to the second aspect to be
enhanced beyond the results obtained with simple
35 admixtures of the two materials making up the
composite, ie fine particulate material and white
insoluble pigment compound (eg precipitated calcium
25 carbonate). The present invention therefore offers
40 an inexpensive way of extending the effectiveness of
the two materials making up the composite.

In the method according to the first aspect of
45 the present invention if additional particulate
30 solids are present, other than consumable reagent(s)
employed to form the precipitate compound, in the

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aqueous medium in which the precipitation reaction is carried out the amount of such solids which may be present will depend on the kind of reactor employed which, in turn, will depend upon the process conditions required to be operated. These are discussed further below. Where step (a) of the method according to the first aspect is carried out in a conventional stirred batch reactor, eg for precipitating calcium carbonate, the said solids may form from 0% to 20% by weight of the aqueous suspension to be treated to give precipitation formation therein. Desirably, such solids constitute from 0% to 10% by weight, especially 0% to 7% by weight, of the treated suspension in the use of such a reactor.

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In other reactors, eg to operate a continuous or semi-continuous process, the solids content may be higher, eg up to levels of 40% or even 50%.

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In the composite pigment material according to the second aspect of the present invention the weight ratio of the said fine particulate material to precipitated white pigment compound present may be in the range 1:100 to 1:1, especially 1:20 to 1:2. The white pigment compound present in the composite pigment material (including any particles present in addition to the fine particulate material) may constitute at least 50% by weight, especially from 70% to 96% by weight of the material (on a dry solids basis).

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The composite pigment material according to the second aspect of the present invention may comprise

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10 particles whose size will depend upon the size of the constituents used to form the particles. If desired, it is possible to treat the composite material particles produced by comminution, eg by wet stirring, milling or grinding, and optionally particle size classification as described hereinafter.

15 The individual precipitate crystals which make up the matrix of the composite pigment material will generally have a size comparable with such crystals formed in the prior art (when not part of a composite structure). Generally, such crystals will be sub-micron size, eg having sizes in the range 0.1 μ m to 1 μ m.

20 15 Where the fine particulate material comprises TiO₂, the TiO₂ particles employed in the method according to the first aspect of the present invention may be of the rutile or anatase form. We prefer the rutile form. Commercially available TiO₂ pigment material may be employed. However, because the problem of retention of TiO₂ in paper making is considerably reduced by forming the composite pigment material according to the second aspect, it is possible although not essential in forming the composite material to use at least a portion of TiO₂ particles which are finer than those conventionally used, eg having a size of about 0.1 μ m or even less.

25 40 In the method according to the first aspect of the present invention, the fresh particles of the fine particulate material may be employed in an aqueous suspension to be treated to form a

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10 precipitate therein may be added in dry form to a reactor vessel containing water or in predispersed slurry form to the reactor vessel. In either case it is preferred that the mixed suspension so formed
5 containing the fine particulate material is mechanically agitated, eg by vigorous stirring,
15 preferably both before and during the precipitation reaction, to ensure that the particles of the fine particulate material are maintained in a dispersed
20 state in the suspension whilst the crystal precipitation proceeds. If desired, a known dispersing agent, eg a polyelectrolyte such as one of the agents well known for the dispersion of
25 particulate materials in an aqueous suspension, eg sodium polyacrylate, may also be present, preferably
15 in a small amount, eg less than 0.5 per cent by weight.

30 The fine particulate material may be added with vigorous mixing to an aqueous lime suspension and the
20 required precipitate may be produced by carbonating the mixed suspension so formed. It is not necessary
35 to incorporate the fine particulate material, or all of that material, prior to carbonating. Some or all of the fine particulate material may be added after
25 some carbonation, ie to produce some of the precipitate crystals. The fine particulate material
40 may be added in more than one dose. Each addition may optionally be accompanied by an addition of lime and followed by a carbonation step.

45 30 If the water employed to provide the aqueous medium (eg to provide the aqueous suspension employed

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in step (a)) in the method according to the first aspect of the present invention contains soluble or insoluble species which will affect the process of precipitation of the white pigment compound it may be desirable to carry out a preliminary precipitation step in the water prior to introduction of the said fine particulate material which will form the composite pigment material together with the white pigment compound. For example, the employed water may be so-called white water from a paper making operation. The preliminary precipitation will entrain the species present in the white water in the manner described in EP 604,095. Up to 90% by weight, eg from 1% to 50%, or 10% to 50%, by weight of the white pigment compound to be formed, may be precipitated in the preliminary precipitation step(s) prior to addition of the fine particulate material. The resulting final product formed will consist of a mixture of particles of the white pigment compound, the fine particulate material and others containing only the precipitate and species originally present in the water used. The product may also contain aggregates of two or more of the various kinds of precipitate particles possible.

As noted above, the precipitated white pigment compound may comprise an alkaline earth metal carbonate, especially calcium carbonate, which may conveniently be produced in a well known way by addition of a carbon dioxide-containing gas to an aqueous medium containing ions of the required alkaline earth metal (as well as the fine particles

5 and the fibres when required). Such production
allows the required white pigment to be produced
10 without substantial undesirable production of non-
crystalline by-products as in the prior art. The
5 aqueous medium may in this case comprise a medium
15 containing a hydroxide of the required alkaline earth
metal. Such a hydroxide may comprise a hydroxide of
one or more of calcium, magnesium and barium.

Where the aqueous medium comprises a hydroxide,
20 10 the hydroxide may be separately prepared and added to
the aqueous medium or alternatively may be prepared
in situ in the aqueous medium, in each case, for
example, by slaking an alkaline earth metal oxide (eg
25 calcium oxide or quicklime, when calcium hydroxide is
15 desired). Where an alkaline earth metal oxide, eg
calcium oxide is to be slaked in an aqueous medium
either separately or in situ in the reactor vessel,
30 the oxide may previously be screened, eg using a
125µm screen, or a 53µm screen, to separate large
20 particles so that these are not present in the
slaking process.

35 Where the aqueous medium comprises calcium
hydroxide produced by slaking in an aqueous medium,
the calcium hydroxide will itself be in the form of a
40 25 suspension in the aqueous medium, ie so called
'slaked lime'. Calcium ions will sparingly enter
solution and will be continuously consumed and
replaced as the precipitation reaction proceeds, eg
45 by addition of carbon dioxide. Preferably, a
30 suspension formed in this way contains between from
5% to 50% by weight of the hydroxide particles.

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Desirably, there is between 0.5 mole and 3.0 moles, especially from 1.0 to 2.0 moles, of the alkaline earth metal hydroxide in the aqueous medium. For slaking of lime, the temperature of the aqueous medium may be from 0°C to 80°C. The temperature will rise during the slaking process. If the aqueous medium is not at the appropriate temperature after slaking, it may be heated or cooled to achieve the desired temperature before further use.

Efficient dispersion and dissolution of the alkaline earth metal hydroxide may also be assisted by agitation, eg by stirring of the aqueous suspension, to provide uniform distribution of the particulate solid material comprising the hydroxide. This agitation may be combined with that applied to the particles of the fine particulate material and the fibres.

The source of the alkaline earth metal ions, eg calcium oxide or calcium hydroxide (where the precipitated compound to be formed is calcium carbonate), may be added to water employed to form the aqueous medium before, during or after the addition of the fine particulate material. Where a batch reactor vessel is employed, we prefer to add the fine particulate material to the reactor vessel after adding a suspension of slaked lime to the vessel. Water may be added after any of the individual addition stages.

Where an alkaline earth metal carbonate is to be precipitated by addition of CO₂ to an aqueous suspension containing a source of alkaline earth

metal ions (and in at least part of the process also fine particulate material) the carbonation reaction may be carried out in a conventional vessel as is well known to those skilled in the art of

precipitated carbonate production. Where the aqueous medium comprises slaked lime, the slaked lime suspension may be prepared in the vessel in which the carbonation is to be carried out, or in a separate vessel prior to introduction to the carbonation vessel.

The addition of a carbon dioxide-containing gas to an aqueous medium containing slaked lime (and, in at least part of the process, also fine particulate material and fibres) may be continued until the pH of the aqueous medium has fallen, eg to a pH less than 9.0 preferably to a pH less than 7.5, eg by monitoring the pH until it falls and then becomes stable. This indicates that all of the alkaline earth metal ions have been consumed, eg by consumption of all calcium hydroxide present.

The reactor vessel in which the precipitation reaction is carried out to produce the composite material according to the second aspect of the present invention may take various forms depending on the process conditions required to be operated as described herein. Reactor vessels known in the prior art for the production of precipitated calcium carbonate from slaked lime and carbon dioxide gas may be employed. The reaction may be carried out as a batch, continuous or semi-continuous process as appropriate.

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In its simplest form, the reaction vessel may be a container in which the various ingredients to be present in an aqueous suspension during the reaction may be added and mixed together in the vessel and CO₂ gas may be bubbled into the mixture.

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The reaction may be carried out as a continuous or semi-continuous process in a cascade of reactor vessels. In such an arrangement an aqueous suspension containing lime, and where required fine particulate material such as TiO₂, may be delivered to the various vessels in sequence and carbon dioxide may be applied to each vessel whereby the required reaction takes place progressively along the sequence.

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Another form of reactor which may be employed for a continuous or semi-continuous reaction is one in which the ingredients of the aqueous suspension and the final reactant, eg carbon dioxide, are mixed together via one or more static mixers of a known kind, eg in a known in-line arrangement. Doses of individual ingredients, eg lime, fine particulate material, or carbon dioxide, as appropriate may be delivered via two or more mixers to give a sequence of ingredient additions whereby the reaction required takes place progressively in stages.

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Preferably, during the reaction, or each stage of the reaction, especially where fine particulate material is present, mixing is applied. Gas such as CO₂ which is applied may be pressurised.

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The aqueous medium in which the alkaline earth metal ions are contained and reacted with

precipitate-forming reagent, eg carbon dioxide, in
the method according to the first aspect of the
present invention may (in addition to fine
particulate material in at least part of the process)
also contain one or more chemicals of a kind known
for use in precipitate production, eg it may comprise
a buffer solution to give the product so-called acid
tolerance or a frothing agent to provide efficient
reaction between CO₂ bubbles and lime, or an additive,
eg an organic additive, eg citric acid, to facilitate
crystal nucleation and growth.

As noted earlier, the aqueous medium in which
the composite pigment material is to be produced in
the method according to the first aspect may, (in
addition to added fresh particles of a fine
particulate material in at least part of the process)
also contain other fine suspended solid material
which may be in addition to any suspension of
consumable particles employed to provide a source of
alkaline earth metal ions. For example, there may be
present other fresh or alternatively previously used
pigment particles and/or fibres. For example, fines
collected from a waste stream from a paper making
process or a waste paper treatment or de-inking
process as described in copending published patent
applications EP-A-604,095 and EP-A-737,774 may also
be present prior to any precipitation step involving
the fine particulate material and, as noted
hereinbefore, may be entrained by precipitation
before the fine particulate material is present or,
alternatively whilst the particulate material is

5 present. Such fines may comprise used particles
10 present in the waste stream such as organic particles
such as ink, latex or polymer particles and/or
inorganic particles such as mineral filler or coating
5 particles as used in paper making or paper coating
and/or fine fibres. Alternatively, or in addition, a
15 selection of particles from a minerals refining or
separation process or residue from an incineration
process, eg incineration of paper de-inking waste,
20 may be present as described in PCT/GB96/00884. Where
such other solid materials are included in the
treated aqueous medium they may be present in an
amount of up to 50% by weight, eg 1% to 10% by
25 weight, based on the dry weight of composite material
product to be formed. Where such other solids are
15 present in the suspension to be treated, such solids
become entrained, together with the freshly added
fine particulate material, and bond to the
30 precipitate crystals formed and thereby form a multi-
media mixed aggregate solid system. The aggregate
20 product so formed is useful in the papermaking and
paper coating applications described below.

Where a carbon dioxide-containing gas is
employed to provide a carbonation reaction in the
40 25 method according to the first aspect, the carbon
dioxide-containing gas may be substantially pure
carbon dioxide eg as commercially supplied in a
compressed gas cylinder or may be present in a
45 mixture with other gases. The supplied carbon
30 dioxide gas may be diluted with other inert gases, eg
air, nitrogen, etc. The carbon dioxide may be

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10 present as a mixture of spent gases such as flue gases, eg obtained from a lime calcination plant in which quicklime is produced for conversion into slaked lime (for use in the process according to the first aspect). The gas may be applied under pressure, eg in the manner described hereinbefore.

15 The temperature of the aqueous medium when the precipitate-containing composite material is formed therein, eg when a carbon dioxide-containing gas is added thereto, is preferably in the range of from 1°C to 80°C, especially 20°C to 60°C, more preferably 30°C to 55°C. Such an aqueous medium may be derived from used water from a paper making plant which may have an appropriate elevated temperature when delivered for use in the method of the present invention.

20 It is known, eg as described in US-A-715,832, that the reaction conditions employed to produce a precipitated calcium carbonate product can be selected to aim for a predominant precipitate crystal form, eg scalenohedral, aragonite or rhombohedral, which will give desired properties, eg brightness, from the crystals when used in paper. Such reaction conditions may be selected and applied in operation of the method according to the first aspect of the present invention. However, since the reaction medium in which the crystals will precipitate in the method of the invention is not a homogeneous one, the crystal form of calcium carbonate achieved in practice in producing the composite pigment material is unlikely to be near to 100% of a selected form. It is quite usual for one crystal form even when

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10 predominant to be mixed with other forms. Such mixed forms will however generally give suitable product properties because the optical properties of the product will not result from the precipitate crystals alone.

15 The addition of a carbon dioxide-containing gas to an aqueous lime-containing suspension (with or without fine particulate material, may be continued until the pH of the aqueous medium has fallen, eg to
20 a pH less than 9.0 preferably to a pH of 7.5 or less, eg by monitoring the pH until it becomes stable. This indicates that all of the alkaline earth metal ions have been consumed, eg by consumption of all
25 calcium hydroxide present.

15 The composite pigment material according to the second aspect of the present invention when produced is preferably obtained in the form of an aqueous
30 suspension which preferably has a viscosity of not more than 500mPa.s (as measured by a Brookfield
20 Viscometer using a spindle speed of 100 rpm) and is preferably a pumpable and flowable slurry.

35 The aqueous suspension comprising the composite pigment material formed as a product in the method according to the first aspect of the present
40 25 invention may be further processed for example by dewatering and/or by subjecting the composite-containing suspension to comminution, eg rapid stirring, milling or grinding by one of several known
45 procedures.

30 As described in EP-A-768,344 such a comminution step may be carried out by attrition grinding. In

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such grinding, the grinding medium employed in the comminution step may comprise one of the hard, inorganic materials well known in the grinding of particulate materials. For example, silica sand having a median particle diameter in the range from about 0.1mm to 4mm, eg 0.2mm to 2mm, is a preferred grinding medium. The grinding medium could alternatively be aluminium oxide, zirconium oxide, hard steel or a mixture of any of these materials.

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When the product comprising the composite pigment material is subjected to a comminution step the pH of the aqueous suspension containing the product being treated may rise, as described in EP 768,344A, eg to pH 11 or more, as free basic material, eg unconverted lime (where lime is used as the source of alkaline earth metal ions), entrapped in the crystalline structure comprising the composite material is released by the comminution. Such a pH level may be undesirable in the applications in which the material may be employed, as described hereinafter, because it is potentially harmful to machinery and to operators who have to process the suspension.

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An additional step to reduce the pH of the aqueous suspension containing the composite pigment material may be applied after a comminution step. The additional step may be applied until the pH falls to a suitable level, eg pH 10 or below, eg pH 9 or below, preferably pH 7.5 or below. The additional step may comprise further treatment by carbonation of the precipitate-containing suspension.

Alternatively, or in addition, a material known for use in reducing the pH of a mineral suspension may be added. Such a material may, for example, comprise a mild mineral acid such as phosphoric acid.

The aqueous suspension containing composite pigment material product formed in the method according to the first aspect of the present invention may be treated so as to separate partially or fully the aqueous host medium from the composite material solids using one or more separation processes which may be known processes. For example, processes such as filtration, sedimentation, centrifugation or evaporation may be used. Filtration using a filter press is usually preferred. The separated aqueous medium, eg water, may, optionally with further purification or clarification by one or more chemical, biochemical or mechanical processes which may be known per se, may be recycled for reuse, eg in a paper mill, eg for use in diluting the paper making stock or for use as showers for washing machinery. The separated solids may be assessed for quality control by measurements taken on samples and subsequently delivered to a storage tank and thereafter supplied as necessary for use in a user application, eg as described hereinbefore. The solids-containing suspension may be re-diluted for use at the user plant.

It is not necessary for an aqueous suspension containing a composite pigment material according to the second aspect of the present invention to be dewatered prior to supply for use in a user

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10 application, eg for use in paper making in a paper mill. The aqueous suspension or slurry may be delivered to a storage tank or directly to the user plant without substantial dewatering.

5 Where the composite pigment material is to be
15 used as a filler in a paper making composition, the composite material may be supplied to the papermaking mill in one of various concentrations in water. The concentration may range from dilute suspension form
20 to dry particulate solids. The composite pigment material after preparation in the method according to the first aspect of the present invention may or may not be treated as appropriate, eg by dewatering or
25 not, so that it may be delivered to the user plant, eg paper making mill, in the required concentration.

15 The extent of dilution or concentration of the form in which the composite pigment material product is added to the user composition, eg paper making
30 furnish composition, does not critically affect the properties of the resulting product, eg paper sheet. It may, however, for economic and practical reasons
35 be more suitable to supply the composite pigment material product in the form of a concentrated pumpable aqueous slurry. Where this product is
25 supplied for use in a process at another location it may be preferable or desirable to dry the product
40 prior to transport. Where the product is supplied to a nearby plant it is likely to be delivered in slurry form. Where this product has been concentrated or
45 dried prior to delivery and subsequently re-dispersed in or diluted with clean water prior to re-use, the

concentration and dilution steps do not materially affect the usefulness of the product.

In any event, where the composite pigment material product is to be used as a pigment filler material in paper making, this product may, as will be clearly evident to those familiar with the paper making art, be used in a well known manner. It may be blended in various proportions with conventional filler materials, eg precipitated or natural, eg ground, calcium carbonate, kaolin or other clay, calcined kaolin, talc, calcium sulfate etc, the ingredients and composition as well as the host cellulosic fibres being selected according to the quality of paper required to be produced. In general, these materials are likely to be in slurry form when they are mixed. The host cellulosic fibres may be any one or more of the forms of fibers employed in paper making. The fibers may be fresh or previously unused fibers, and/or recycled fibers obtained from a used source, eg broke.

The paper maker will normally select the concentration of the composite pigment material (produced in accordance with the present invention) used in aqueous suspension form and the delivery rate of the suspension at the point of addition to the paper making composition, eg furnish. As noted above, this may require re-dilution of a suspension which has been delivered to the paper mill in concentrated form. Generally, the composite pigment material may form up to about 40%, usually up to about 30%, by weight of the solids content of the

5 paper making composition on a dry weight basis.

10 Where other fillers also form part of the filler

content of the paper making composition a total

filler composition of up to 40% by weight of the

5 solids content of the paper composition may be

15 employed. The composite pigment material according

to the second aspect may form from 1% to 100% by

weight of the added filler on a dry weight basis.

Production of a paper sheet using the paper making

10 furnish is, of course, carried out in a well known
manner.

Where the composite pigment material according

to the second aspect of the present invention is to

25 be employed as a pigment material in a paper coating

15 composition, the composition will generally comprise

an aqueous suspension of pigment, including the

composite pigment material according to the second

30 aspect and optionally other known ingredients, mixed

together with a hydrophilic adhesive and optionally

20 other known ingredients. The composite pigment

material employed in the composition may be mixed

35 with one or more conventional pigments, eg as

described above. The adhesive may form from 4% to

30%, especially 4% to 15%, by weight based on the

25 total dry weight of pigment or pigments present. The

40 adhesive may be one of the known paper coating

adhesives employed in the art, eg chosen from the

group consisting of starches, proteinaceous adhesives

45 such as casein and latices of, for example, styrene

30 butadiene rubbers and acrylic polymers.

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The paper coating composition may also include one or more of the various well known optional additives conventionally used in paper coating compositions, eg a thickener, eg in an amount of up to 2% by weight based upon the total dry weight of pigment or pigments present, up to 1% by weight of a soluble binder, a lubricant, eg sodium stearate forming 0.5% of the weight of pigment present, and/or soluble binder and/or an insolubiliser forming up to 1% by weight of binder present.

The paper coating composition may be formed by mixing together an aqueous dispersed suspension of the composite pigment material optionally with one or more further aqueous dispersed suspensions containing other pigments, with the adhesive and any other optional constituents, eg thickener and/or lubricant and/or soluble binder and/or insolubiliser, in a manner familiar to those skilled in the art. Use of the coating composition formed to coat a paper or other sheet material is of course carried out in a well known manner, eg using one of the many coating machines employed in the prior art.

Precipitation of calcium carbonate in a fines-containing aqueous waste suspension, eg obtained from a paper making waste stream, is described in EP-B-658,606. The aqueous suspension in the process described therein may contain waste fines which include fine fibers and fine inorganic materials which may incidentally include a very small concentration of TiO_2 particles or other fine particulate materials. However, generally, since

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10 these fines are used materials, they may have been
produced from a variety of waste streams and
therefore may be of variable composition and
concentration, and they are not suitable to provide
5 (on their own) sources of the fine particulate
material of the quality required of the fresh
15 particles of the fine particulate material as used in
the present invention. Fine particulate material
such as TiO_2 derived from such waste streams will
20 generally be agglomerated and coagulated because of
the presence of a variety of polymeric chemical
additives in the waste stream and will not therefore
show the benefits obtained by forming the novel
25 composite pigment material (according to the second
aspect of the present invention) from fresh particles
of fine particulate material and bonded precipitated
white pigment compound such as CaCO_3 as described
30 hereinbefore. However, as noted above, it is
possible that the aqueous medium employed in the
20 method according to the first aspect of the present
invention may optionally contain such fines as an
35 additional solids component which will then
constitute part of the composite pigment material
produced.
25 Embodiments of the present invention will now be
described by way of example only with reference to
40 the following illustrative Examples and with
reference to the accompanying drawings, wherein:

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing, for three different samples of composite pigment material embodying the invention, scattering coefficient of paper sheets incorporating each sample as filler plotted against the percentage by weight of filler (pigment) in the sheets.

Figure 2 is a graph showing, for a sample of composite pigment embodying the invention and in comparison a sample of untreated TiO_2 in admixture with calcium carbonate, % retention of TiO_2 in a paper sheet incorporating each sample as filler plotted against the percentage by weight of filler (pigment) in the sheets (obtained by incineration as described later).

In the following Examples, the properties of samples of composite pigment material embodying the invention were investigated. The samples, designated Samples A, B and C, were prepared as follows.

SAMPLE A

To a stirred 5 gallons reactor, 11.4 liters of water were added. The stirrer speed was 500rpm. 1400 grams of lime were slowly added and the temperature was kept constant at a temperature of about 38°C throughout the addition. The lime was slaked for 1 hour and 10 minutes. After slaking the reactor stirrer speed was increased to 700rpm and 6.24 grams of citric acid were added followed by the addition of 266.67 grams of titanium dioxide. To this agitated slurry, we introduced CO_2 at a rate of

2.52l/min and compressed air at a rate of 8.0l/min.
This started the carbonation of the slurry. The
reaction was carried to completion.

SAMPLE B

To a 5 gallon reactor stirred at 700rpm, we
added 2841ml of a 17.6% by weight precipitated
calcium carbonate slurry. This slurry was carbonated
for a few seconds and then we added 100 grams of
dispersed titanium dioxide and 2758ml of a slaked
lime slurry. The slaked lime slurry had a solids
concentration of 12.5% by weight. The mixture was
then further carbonated by adding CO₂ at a rate of 6.0
litres per minute. The carbonation was carried to
completion.

SAMPLE C

To a stirred (500rpm) 5 gallon reactor, we added
11.4 liters of water. Lime (1400 grams) was added
very slowly in order to maintain the reactor
temperature at about 38°C throughout the addition of
the lime. The total slaking time was 1 hour and 10
minutes. After slaking was completed, the stirrer
speed was increased to 700rpm and 6.24 grams of
citric acid were added. Carbonation was started by
bubbling CO₂ at a rate of 2.52l/min and compressed air
at a rate of 2.52l/min through the stirred slurry in
the reactor. Half way through carbonation, we added
266.67 grams of titanium dioxide. The reaction was
carried to completion by continuing the addition of
carbon dioxide and compressed air.

In addition, for comparison purposes, the following Sample D was prepared using a procedure known in the prior art.

SAMPLE D

A pcc product was prepared in the manner of Sample B, except that no TiO_2 was employed during the course of the pcc production procedure. Subsequently, TiO_2 was admixed with the TiO_2 to give a mixture of TiO_2 and pcc in a weight ratio of 10:90, the same target weight ratio in the composite product, Sample B.

EXAMPLE 1

Handsheets were made with different filler levels using the standard procedure described in TAPPI Test Method 205. The fillers used in preparing the handsheets were separately Samples A, B and C. The furnish used in making the handsheets was a 50/50 blend (by weight) of soft and hard wood fibers from Weyerhaeuser, Prince Albert, Canada. The sheet formation was kept constant at around 130, as measured by a Paprican Micro-Scanner made by OpTest Equipment Inc. The sheet grammage was kept at around 75gsm⁻². The optical properties of the sheet were measured by an instrument produced and supplied under the tradename Technibrite Micro TB-IC by Technidyne Corporation. The scattering coefficients were calculated using Kubelka-Munk equations as in the manner described in EP-A-604,095. The results

obtained for Samples A, B and C are plotted as curves labelled respectively A, B and C in Figure 1.

It can be clearly seen from Figure 1 that the composite pigment material made by introducing the titanium dioxide during the carbonation step had higher scattering coefficients than the others although all three materials show beneficial scattering curves.

EXAMPLE 2

The zeta potentials of composite Sample B and separately titanium dioxide were measured at different pH values utilizing a charge analyzer manufactured by SKS associates. The results are given in Table 1 as follows.

TABLE 1: Zeta Potential

	pH7.0	pH8.0	pH9.0
Sample B	24	21	24.9
TiO ₂	-80.8	-79.2	-81.7

Table 1 shows that in contrast to TiO₂ untreated, the TiO₂-CaCO₃ composite of the invention, Sample A, has a positive charge potential in its surface. This quality makes it easier to the papermaker to retain the pigment in the sheet.

EXAMPLE 3

Handsheets were prepared using the same procedure as in Example 1. The filler pigments used

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10 in this Example 3 were separately Sample B and Sample D. Furthermore, headbox pads were obtained during the experiments, so that the retention of the fillers could be measured in a known manner. The sheets were

5 15 incinerated at 500°C and 950°C and the weight of ash remaining was measured. This allowed us to calculate the weight percent titanium dioxide in the sheets.

(The loss in weight between 500°C and 950°C allows the weight of CaCO₃ present to be determined.) The

10 20 results are plotted in Figure 2 in which a curve labelled B represents Sample B and a curve labelled D represents Sample D.

25 15 As can be readily seen from Figure 2, the titanium dioxide retention in the composite pigment embodying the invention, Sample B, is higher than in the mixture Sample D. In fact an increase of approximately 200% can be observed.

Claims

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CLAIMS

1. A method of preparing and using a composite pigment material which incorporates a fine particulate material, which method comprises the steps of: (a) treating an aqueous medium containing dispersed particles of a fine particulate material by chemically reacting therein a first reactant and a second reactant to precipitate therein crystals of a white insoluble pigment compound thereby forming in the aqueous medium a composite pigment material comprising a composite matrix of precipitated crystals of the white pigment compound and particles of the fine particulate material dispersed and bonded within the matrix wherein the first and second reactants are such that they react together without producing a substantial amount of non-crystalline by-product; and (b) adding the composite material to a composition for forming or coating a fibrous sheet material.
2. A method as claimed in claim 1 and wherein the fine particulate material and the first and second reactants employed to produce the precipitation reaction are obtained from separate stocks.
3. A method as claimed in claim 1 and wherein at least part of the fine particulate material is fresh material which has not previously been used in an industrial operation.
4. A method as claimed in claim 1 and which includes the step (c) of making or coating a fibrous

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10 sheet material using the composition produced in step (b).

5. A method as claimed in claim 4 and wherein the sheet material comprises paper, paper board, card, cardboard or the like.

6. A method as claimed in claim 1 and wherein the white pigment compound comprises one or more alkaline earth metal compounds.

7. A method as claimed in claim 6 and wherein the white pigment compound comprises calcium carbonate.

8. A method as claimed in claim 1 and wherein the precipitation reaction is carried out in a batch reactor.

9. A method as claimed in claim 1 and wherein the method is carried out as a continuous or semi-continuous process.

10. A method as claimed in claim 1 and wherein the aqueous suspension is mechanically agitated before and during the precipitation reaction.

11. A method as claimed in claim 1 and wherein at least one preliminary precipitation reaction is carried out in the aqueous medium from which the aqueous suspension employed in step (a) is produced, prior to the fine particulate material being present therein.

12. A method as claimed in claim 11 and wherein the fine particulate material is added to the aqueous medium in multiple doses, a precipitate reaction stage following each such addition.

13. A method as claimed in claim 1 and wherein the white pigment compound comprises calcium carbonate

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10 and is obtained in the composite pigment material by including in the aqueous suspension, together with the fine particulate material in at least a part of the process, calcium hydroxide, and passing a carbon dioxide-containing gas into the aqueous medium to provide precipitation of the calcium carbonate by reaction of the calcium hydroxide and carbon dioxide.

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20 14. A method as claimed in claim 13 and wherein the carbon dioxide-containing gas is added until the pH of the aqueous suspension falls to a value of 7.5 or less.

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30 15. A method as claimed in claim 1 and wherein the aqueous medium which is treated to form the white pigment compound by the precipitation reaction comprises, in addition to the fine particulate material, any consumable solids required as reactant to produce the precipitate, additional solid fines derived from a waste stream, the fines optionally being treated by a preliminary precipitation step prior to treatment in step (a).

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40 16. A method as claimed in claim 1 and wherein the temperature of the aqueous suspension when the composite pigment material is being formed by the precipitation reaction therein in step (a) is in the range 20°C to 60°C.

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50 17. A method as claimed in claim 1 and wherein the composite pigment material is further treated before addition to the paper making or paper coating composition, the further treatment comprising one or more of dewatering, comminution, pH adjustment and re-dilution.

5
10 18. A method as claimed in claim 1 and wherein in step (b) the composite pigment material is added to other pigment materials during the production of the paper making or paper coating composition.

5 19. A method as claimed in claim 1 and wherein the composite pigment material is added to the paper making or paper coating composition in an amount which will provide from 1% to 100% by weight of the pigment present in the paper making or paper coating composition.
10

20 20. Composite material for use as a pigment material in paper making or paper coating which composite material comprises a composite matrix of precipitated crystals of an insoluble white pigment compound and
25 15 particles of a fine particulate material, other than the precipitated crystals, dispersed and bonded within the matrix, the composite material being a product of treating an aqueous suspension of dispersed, fresh particles of a fine particulate
30 20 material by chemically precipitating the white pigment compound in the suspension in a reaction substantially free of by-products.
35

40 21. A composite material as claimed in claim 20 and wherein the fine particulate material comprises TiO_2 and the white pigment compound comprises calcium carbonate.
25

45 22. A composite material as claimed in claim 21 and wherein the weight ratio of TiO_2 to calcium carbonate in the material is in the range of from 1:100 to 1:1.
50
55

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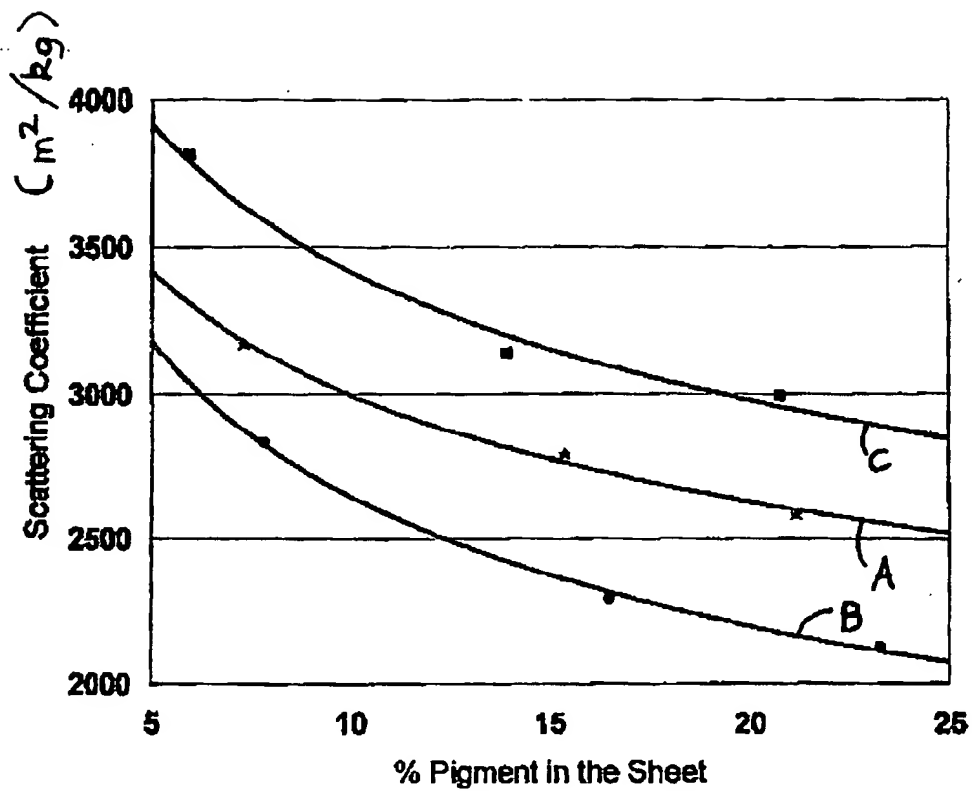


Figure 1

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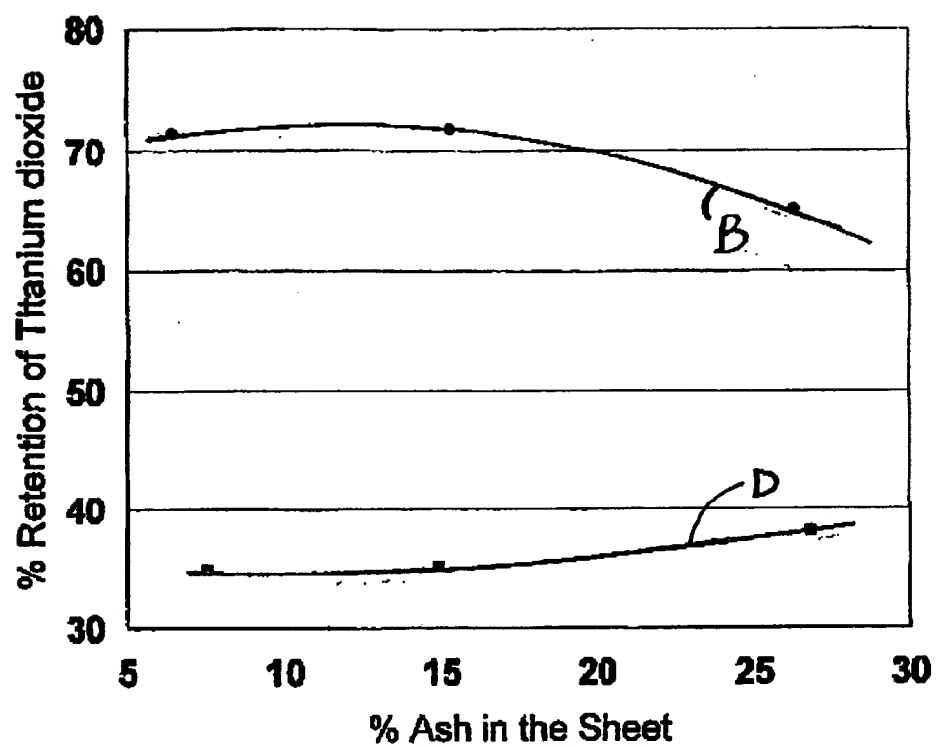


Figure 2

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 00/16610

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09C1/00 D21H17/69 D21H19/38		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09C D21H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 886 069 A (BOLT JOHN DAVIS) 23 March 1999 (1999-03-23) the whole document	1-22
P, A	WO 99 51691 A (ECC INT INC) 14 October 1999 (1999-10-14) claims 1-4	1-10
A	EP 0 892 019 A (ECC INT LTD) 20 January 1999 (1999-01-20) cited in the application claims 1-17	1-22
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 26 October 2000		Date of mailing of the international search report 03/11/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer: LIBBERECHT, E

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 00/16610

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 014, no. 215 (C-0716), 8 May 1990 (1990-05-08) & JP 02 051419 A (KOMESHIYOU SEKKAI KOGYO KK), 21 February 1990 (1990-02-21) abstract -----</p>	1-22

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Form PCT/ISA210 (continuation of second sheet) (July 1992)

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